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Final Report on "A Continuous Thermometric Apparatus for Carbon Monoxide Detection"
to
June 28, 1943
by
Dr. J. H. Yoe

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Report OSRD No. 1743

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Section 3

Final Report on "A Continuous Thermometric Apparatus for Carbon Monoxide Detection"

Service Directives NA-106, AC-59

Endorsement (1) From Dr. Warren C. Johnson, in charge of section to Dr. W. R. Kirner, Chief, Division 9.

Forwarding report and noting:

"An apparatus has been developed for the determination of carbon monoxide and air mixtures ranging in concentration from 0.01 per cent to 0.1 per cent and higher, if necessary. The principle of the apparatus is dependent upon the heat developed when carbon monoxide reacts with oxygen on a hopcalite surface. The heat liberated is proportionate to the concentration of carbon monoxide and is determined by a specially designed mercury thermometer which contains a number of platinum wire contracts along the mercury thread. Several different types of indicating devices which may also be used as warning devices are connected to the platinum contacts so that it is possible to determine at any given time the approximate concentration of carbon monoxide. These contacts are placed at such points as to indicate a change in the carbon monoxide concentration of about 0.01 per cent. The lower limit of sensitivity of the apparatus is about 0.01 per cent. The apparatus is simple in construction, unusually easy to operate, entirely automatic in operation, and, in addition, requires little servicing. Although it is limited in its sensitivity, the apparatus might well be used in a number of places where appreciable amounts of carbon monoxide might be found. The apparatus fulfills the original requirements set up for a carbon monoxide instrument as far as concentration limits are concerned."

(2) from Dr. W. R. Kirner, Chief Division 9 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

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This is a final report under Contract 9-344, OEMsr-139 with the University of Virginia.

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A Continuous Thermometric Apparatus
for Carbon Monoxide Detection

John H. Yoe and Charles H. Lindsley

University of Virginia

A B S T R A C T

A simple apparatus is described which will indicate, by a variety of means, the presence of carbon monoxide in concentrations greater than certain specified values. This is accomplished by means of a mercury-in-glass thermometer with several platinum contacts sealed into the capillary. The thermometer is placed in a small cell containing Hopcalite, and a stream of air(1.5 liters per minute) passes through the catalyst and around the thermometer bulb. The cell in turn is enclosed in an electrically heated thermostat controlled by a Fenwal thermoswitch with a constancy of about ± 0.1°C. A green signal light and battery are connected to the lowest and second contacts of the thermometer, and the temperature of the thermostat is set so that at thermal equilibrium the second contact is just closed by the mercury thread; the green light therefore is always on when the apparatus is ready for use. The higher contacts are spaced to correspond to certain temperature increments above this base temperature, and these increments are those resulting from the heat of oxidation on the Hopcalite of selected concentrations of carbon monoxide. Thus in one thermometer used the base temperature was 50.0°, the third contact was at 50.5°, and the fourth at 52.5°. A rise in temperature of 0.5° is produced when the air passing over the catalyst contains 0.01% CO; 2.5° corresponds to 0.05%. Various warning devices may be connected to these higher contacts and will be activated when carbon monoxide is present in these concentrations (or higher). Three types of such devices have been assembled and are described: one involves a series of colored lights, another uses a microammeter, while the third consists of two high-sensitivity relays which may be used to perform a variety of operations. It is clear that the base temperature of the thermostat and the temperature increments to be measured can be selected within wide limits simply by specifying the position of the several contacts when the thermometers are made. Hence the apparatus can be used under many different conditions to determine a wide range of concentrations, although the concentrations at which any particular thermometer may be used are limited. Since it would be impractical to attempt to put the

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contacts closer to each other than about 0.5°, the concentration of carbon monoxide could only be determined in steps of about 0.01%.

The thermostat itself is about five inches square and eight inches high, and weighs less than five pounds. The weight and dimensions can be further reduced. The heating element consumes about 30 watts; for an ambient temperature of 18°C., it is on less than half the time. Wide variations in the impressed voltage (20 to 30 volts) have little effect on the temperature maintained within the thermostat. Before reaching the catalyst cell the air stream passes through a 20-foot coil of copper tubing in order to bring it to the base temperature. Even with external temperatures as low as -40° and rates of flow of three liters per minute, this preheating is adequate.

In spite of some limitations, which are discussed in the report, the apparatus does possess the following important advantages: it is simple, easy to operate, fully automatic; it requires little servicing; and it is readily adaptable to a wide variety of warning and protective devices.

A Continuous Thermometric Apparatus for Carbon Monoxide Detection

John H. Yoe and Charles H. Lindsley
University of Virginia

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A Continuous Thermometric Apparatus for Carbon Monoxide Detection

INTRODUCTION

Our report[1] of May 15, 1942 described a simple apparatus for measuring the concentration of carbon monoxide in air. The air was drawn through a small quantity of Hopcalite, on which the carbon monoxide was oxidized, and the rise in temperature resulting from the heat of oxidation was measured by a thermometer. A calibration curve and chart permitted the observer to estimate the concentration of carbon monoxide within three to four minutes, for a rate of air flow of 1.5 liters per minute. The apparatus was simple, inexpensive, and easy to operate. Concentrations of carbon monoxide between 0.01% and 0.2% (or even higher) could be determined with an accuracy of about 0.005%. (Many details regarding the history, nature, and behavior of Hopcalite, together with references to the literature, are given in the report of May 15, 1942 and will not be repeated here.)

Although this apparatus has several advantages, especially for laboratory use, it also possesses serious disadvantages, particularly for field work. Thus it was essential that the ambient temperature remain very nearly constant during the test and also during the preceding five or ten minutes when the apparatus was being brought to the ambient temperature, if not already at it. This requirement made the apparatus relatively useless for flight test work in airplanes, where the temperature changes rapidly. Also for many important applications it was not practical for an observer to read the thermometer. Finally the apparatus could not be used as a continuous indicator unless its temperature and that of the air reaching the catalyst remained constant to within 0.2°C. for the duration of the test.

It will be seen that these objections would be overcome if means were provided for maintaining the temperature of the apparatus and of the incoming

1. Formal Progress Report, OSRD No. 748.

air at a constant value, and if some way were provided to "read" the thermometer automatically. The apparatus here described attempts to do these two things. The catalyst is enclosed in a carefully controlled thermostat, and the entering air passes through a copper coil also enclosed therein. The reading of the thermometer is circumvented by sealing platinum contacts into the capillary at points corresponding to desired temperatures; when the mercury thread reaches one of these, the fact can be signaled by a variety of electrical means. These alterations will now be described in detail.

THE THERMOSTAT

The arrangement of thermostat, catalyst cell, and thermometer is shown schematically in Figure 1. The over-all dimensions are 4 3/4 x 5 1/2 x 8 inches, including insulation, and the weight is under 5 pounds (these could be reduced without affecting adversely the operation). The thermostat itself is made of 22 gauge copper, tinned on the inside. Around it are wound, to within half an inch of the top and bottom, two lengths of enameled resistance wire, the walls and the wire being separated by a thin coating of insulating resin. These wires form two heaters, and by means of a suitable switch three heating circuits are therefore possible: the two units in series, the two in parallel, or either one alone. The resistance of each heating element is 9.6 ohms. With a 24-volt source, either unit alone or the two in series may be used. The wire-wound box is insulated thermally by 1/2 inch felt. (Two of these thermostats were made for us by the Leeds and Northrup Company of Philadelphia).

The temperature is controlled by means of a Fenwal thermoswitch which is fitted tightly against the center of one wall. A strip of sheet copper is bent around the thermoswitch and soldered to the wall on each side;

this ensures good thermal contact. The switch therefore maintains the temperature of the walls at a nearly constant value. When the two heating elements are operating in series on 24 volts, the heater is on for about a minute and a half (thermostat temperature 51°C., ambient temperature 25°C).

Figure 2 shows the arrangement of the front panel of the plywood cabinet in which the thermostat is enclosed. Across the top are three toggle switches for the heating circuits: the first is OFF - ON; the second, marked HIGH - LOW, permits use of one unit or of the two in series; the third, INTERMITTENT - CONTINUOUS, enables the operator to short out the thermoswitch when desired. A pilot light indicates when the heater is on. Below the pilot light is a socket in which the four leads from the thermometer terminate.

The closeness of temperature control was determined by means of a thermocouple, one junction of which was embedded in the catalyst. Over a period of several hours the temperature fluctuates over a range of 0.2 - 0.3° (i.e. $\pm$ 0.1 - 0.15°). When the heater is turned off at the end of a day and on again the next morning, the thermostat returns to the same equilibrium temperature. This demonstrates that the setting of the thermoswitch is not changed by undercooling. However, the setting is altered if the temperature rises several degrees above the temperature for which the switch is set. Thus in one test the equilibrium temperature was 50.8°; by shorting out the thermoswitch for 30 minutes (heater on HIGH at 20 volts) the temperature was raised to a maximum of 62°. The heater was then turned off, and the thermostat cooled to 40°. Upon reheating in the normal way, a new equilibrium temperature of 51.7° was observed. While the degree of overheating may seem small to have caused so large a change in the setting of the thermoswitch, it should be noted that because of its position the Fenwal switch takes much more nearly the temperature of the walls than that of the air in the thermostat or of the catalyst (the temperature of which after overheating was found to be 62°); the maximum temperature of the switch, therefore, was undoubtedly considerably higher than 62°. In this connection it may be observed that after the heater is first turned on, the thermoswitch cuts off, indicating that it has reached the temperature for which it is set (51°), when the temperature recorded inside the thermostat has only reached 38°.

A small overshoot can be tolerated without changing the setting of the thermoswitch. Use is made of this fact, in laboratory practice, to reduce the heating-up period. If the heater is simply turned on LOW, about an hour and a half are required to bring the thermostat to equilibrium (24° to 51°). But the following sequence may be followed: switch heater on HIGH; as soon as the pilot light indicates that the heater is off (about ten minutes), short out the thermoswitch, and overheat on HIGH for three two-minute periods, interrupted for one minute between each; then cut in the thermoswitch and set the heater on LOW. In this way the heating-up period can be reduced to about half an hour. Because the overheating periods are short, the setting of the thermoswitch is not changed.

Changes in the impressed voltage do not greatly affect the temperature in the thermostat. Thus when the voltage was 21 v., the equilibrium temperature was 50.7°. When the voltage was changed to 30 v., the equilibrium temperature was raised to 51.0°. Finally, when the voltage was lowered to 20 v., the temperature dropped down to 50.7°.

When the heater is operated on HIGH, the equilibrium temperature is about the same as when operated on LOW, but in the former case the fluctuations are greater. For example, in one test on HIGH the temperature varied between 50.1° and 50.6°, but on LOW the variation was between 50.4° and 50.6°. These observations were made when the room temperature was about 25°, and the LOW heat was entirely adequate. However, if the external temperature should be very low, the reverse situation would probably prevail, and a more nearly constant temperature would be maintained on HIGH than on LOW. In such a case, it would probably be advisable to connect the two heaters in parallel for HIGH, and use a single heater for LOW.

Tests in this laboratory have been carried out with room temperatures ranging from 18^{o} to 34^{o}, and no effect of external temperature on the equilibrium temperature has been observed. The Leeds and Northrup Company has tested similar thermostats at -40^{o} C., and reports that the same temperature is maintained within the thermostat and, further, that the cold incoming air is warmed to this temperature by passage through the copper coil at rates of flow up to at least three liters per minute.

THE CATALYST HOLDER AND THE CATALYST

The catalyst cell is mounted in the following way (see Figure 1): To the bottom of the thermostat is fastened a cylindrical aluminum base. To this base is connected one end of the copper coil. The upper portion of the base is reduced in section as shown to accommodate a thin steel cylinder (turned from a piece of ordinary 3/4 in. pipe). The two ends of this cylinder are left about 1/8 in. thick to give good closure against gaskets set in grooves in the head and base pieces. The rest of the cylinder is turned down to something less than 1/16 in. thick — as thin as possible without entailing possible collapse when the unit is tightened together. The catalyst holder is a thin copper tube about 3/8 in. in diameter with a bottom of 60-mesh brass screen. This tube is held in the steel cylinder by means of a tightly fitting cork ring. The head is similar to the base; an opening is provided in which the leads from the thermometer are sealed, and there is also a connection for the outlet tube. In this outlet may be located an orifice for governing the rate of gas flow for a specified vacuum head to be applied. The head, cylinder, and base are held together in a gas-tight assembly by means of three 1/8 in. steel tie-rods. It would be a definite improvement if some bayonet-type of connection were substituted for the tie-rods.

The specific materials used for these various parts are not important; low heat capacity, good conductivity, and low weight are the chief specifications. At one time the whole unit, except for the tube holding the catalyst, was made of Catalin plastic, with a view to insulating thermally the catalyst and thermometer from the thermostat. Such insulation, however, very greatly increased the time required to bring the apparatus to thermal equilibrium, and when metal was substituted for the plastic, no appreciable decrease in the temperature rise due to oxidation of carbon monoxide was observed. Evidently the air space separating the catalyst tube and the surrounding cylinder provides adequate insulation.

The catalyst charge is one gram of M. S. A. Hopcalite, instrument grade, 18-20 mesh. The life of each charge is greater in this apparatus than in the one previously described (our report dated May 15, 1942) because of the elevated temperature. Drying of the incoming air is effected by means of a tube containing calcium chloride with a layer of indicator Drierite at the end. If the drier is replaced as soon as the indicator begins to change color, a single charge of Hopcalite has been found to remain active for at least a week on continuous operation with air or air containing carbon monoxide.

As was shown in the previous report, because of the high activity of Hopcalite, the temperature attained by the thermometer due to oxidation of carbon monoxide is not significantly different for any rates of gas flow between one and two liters a minute. Below a liter a minute, low rises are encountered because the rate of heat dissipation is large compared to the rate of heat generation. A rate of flow much above two liters per minute is apt to blow the catalyst out of the cell, and also the increased amount of heat liberated is offset by the increased amount of air to be heated. The rate of 1.5 liters per minute has therefore been chosen as the one most practical, but considerable variations from this rate can be tolerated without appreciable effect on the temperature change.

THE THERMOMETER

Thermometers were made to our specifications by the Accuracy Scientific Instrument Company of Philadelphia; the design is shown in Figure 1. Since with this sort of thermometer it is apparent that only a few predetermined temperatures can be "read", a certain amount of arbitrariness entered into the selection of these points. The first temperature to be chosen is the base temperature at which the thermostat is to be maintained. This was chosen as 50° C., since it was high enough to be above any but the very highest ambient temperatures that were anticipated, and yet low enough for the energy consumption to be small. It is clear that if prevailing temperatures near or above 50° C. are to be encountered, the thermostat temperature must be correspondingly raised. The second contact of the thermometer is therefore so placed that the mercury thread reaches it just when the temperature of the thermostat is 50° C., and the thermoswitch is also set for this temperature. (The lowest contact can be inserted at any convenient point between the bulb and the second contact.)

The positions of the third and fourth contacts obviously depend upon the temperature intervals above the base temperature that it is desired to measure, and these in turn depend upon the concentrations of carbon monoxide it is desired to detect. For demonstration purposes, two concentrations were rather arbitrarily selected in setting specifications for the manufacturers of the thermometers: the third point at 50.5° (corresponding approximately to 0.01% CO) and the fourth at 52.5 - 53.0° (corresponding to 0.05 - 0.06% CO). It is clear that for other concentrations other temperatures could equally well be selected; it probably would not be practical or significant, however, to attempt to place the contacts closer than about 0.5°, and the number of contacts that could practically be sealed in any one thermometer is also definitely limited.

Early in the investigation the attempt was made to make the complete apparatus dependent upon a single source of electricity. To this end various circuits were tried in which the 12 or 24 volt source used in the heating circuit also operated, through proper resistances, the several warning devices connected to the contact thermometer. Even on 12 v. it was soon found that some of these arrangements caused sufficient arcing in the capillary to foul the contacts and mercury and hence to render them useless, and in the rest of the arrangements tried there were grounds for suspicion that similar fouling might also take place, though more slowly. Furthermore, with the storage batteries used, there was enough difference in the effective voltage when the heater was on and when it was off to affect very sensibly the operation of the signaling devices. To such effects would be added those due to changes in line voltage to be expected in many service applications. For these reasons the attempt to use a single source was abandoned, and all the devices described below operate on single-cell flashlight batteries. Under these conditions no trouble due to fouling in the thermometer has been experienced.

SIGNALING DEVICES

The multiple-contact thermometer can, of course, be connected with a wide variety of instruments to indicate when the various contacts are closed, i.e., when the specified concentrations of carbon monoxide are passing through the apparatus. Three types have been constructed and their essential parts are represented schematically in Figures 3, 4, and 5. A four-lead socket is mounted in each unit with connections as shown. Any unit could therefore be connected to the thermometer through the corresponding socket in the thermostat panel (Figure 2) by means of a four-wire cable with a four-prong plug at each end.

The first unit (Figure 3) consists simply of three colored lights, each operating on a flashlight battery. The green light comes on when the second contact is closed, indicating that the catalyst is up to temperature and that the apparatus is therefore ready for use; it remains on continuously. For this reason a better source than a small battery should be used. For this light one of the better arrangements using the 12 or 24 v. source could be used, since the contact is closed and opened only when the thermostat is first heated up or finally allowed to cool down. As is evident from the diagram and the previous discussion, the orange light comes on when the air passing through the apparatus contains at least 0.01% carbon monoxide, while the minimum concentration required to turn on the red light is 0.05%.

Figure 4 shows a very satisfactory arrangement. A microammeter and battery are connected through a series of high resistances. The total arc which the needle tranverses is divided into four sections, with distinctive colors, and the resistances are so chosen that as the contacts in the thermometer are closed, the needle stands successively over the center of each section. It is clear that the total current consumption is very low and that the life of the battery consequently is long. Also the resistances and microammeter can be mounted in a standard opening of any instrument panel.

The third device (Figure 5) can itself be adapted to a wide variety of applications. The signal for the second contact is a green light just as in the first device, and the modification suggested there applies equally here. The two higher contacts are connected to two high-sensitivity relays. (Model 28XAX033, supplied by Struthers Dunn Inc., Philadelphia, Pa.) These relays require only 0.008 watt to activate the coils, and the contacts are rated to carry 2 amps. at 115 v. a. c. or 1/4 amp. at 115 v. d. c. About 100 ohms resistance is connected in series with the battery and coil, increasing the life of the former. Of course, relays may be used to operate many signaling devices such as bells and lights or to operate various protective devices such as opening ventilators or turning on fans.

All of these devices have been operated successfully. When air containing 0.01% CO passes through the apparatus, the second signal (orange light, etc.) is given within eight to twelve minutes. The third signal is given within about the same period with air containing 0.05% CO. The variation in time required is probably due to the fluctuations in the temperature of the thermostat already mentioned; these fluctuations narrow or widen the temperature interval that must be closed.

CRITICISM

The apparatus herein described possesses several disadvantages which, it is felt, could be corrected in part at least, should construction of further models be desired. The chief among these is that the method of indicating the temperature is too inflexible. Thus, for example, if enough carbon monoxide were present to raise the temperature 0.49° instead of 0.50°, the interval between the second and third contacts, no signal would be given and the response would be no different from that if pure air were present. Similarly, if the orange signal were on, but not the red, the observer would only know that carbon monoxide was present in concentration greater than 0.01% but less than 0.05%. The disadvantage could be overcome in part by putting contacts closer together, especially if the probable range of concentration is not large. A similar difficulty arises with regard to the setting of the regulator for the thermostat temperature: when the green light is on, the operator knows that the temperature is at least 50.0°, but there is no direct way of making sure that the temperature is not several tenths of a degree higher. The difficulty could be overcome partially by placing a thermometer within the thermostat so that the equilibrium temperature could be checked from time to time.

CONCLUSIONS

In spite of these disadvantages, however, the apparatus does possess the following important advantages: it is simple, easy to operate, fully automatic; it requires little servicing; and it is readily adaptable to a wide variety of warning and protective devices.

The experimental work was performed by Dr. Charles H. Lindsley.

June 28, 1943

Submitted by Dr. J. H. Yoe

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Thermometric Apparatus for Determining Carbon Monoxide with Multiple-Contact Mercury Thermometer

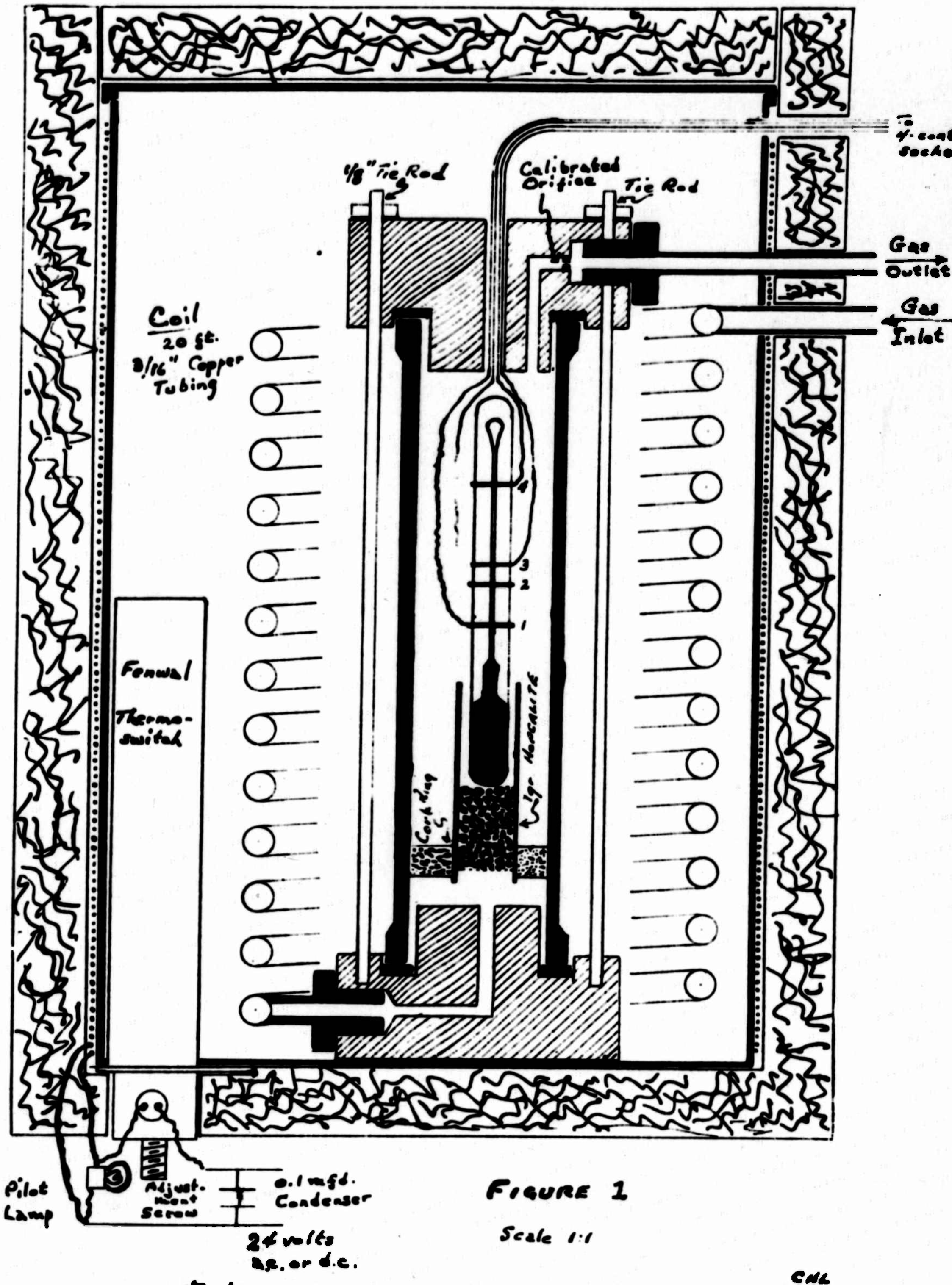

FIGURE 1

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Front Panel of Apparatus

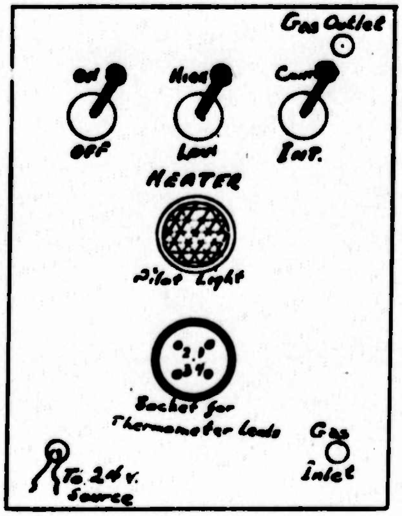

FIGURE 2

Signal Unit I
Colored Lights

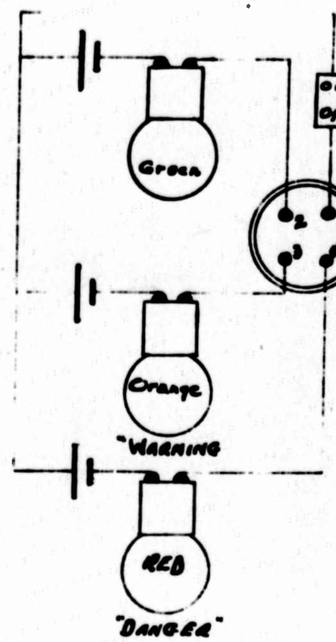

FIGURE 3

Signal Unit II
Micro-ammeter

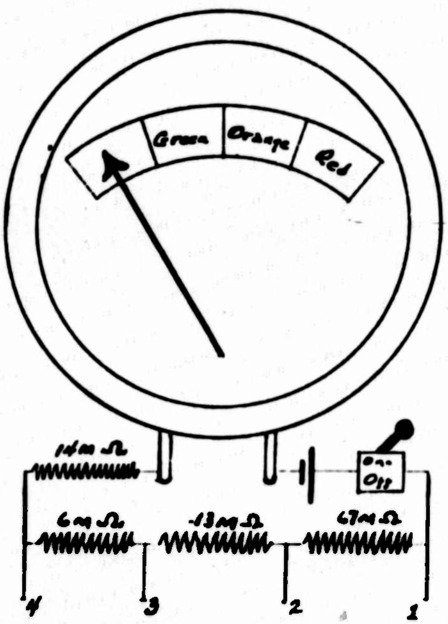

FIGURE 4

Signal Unit III
High-Sensitivity Relays

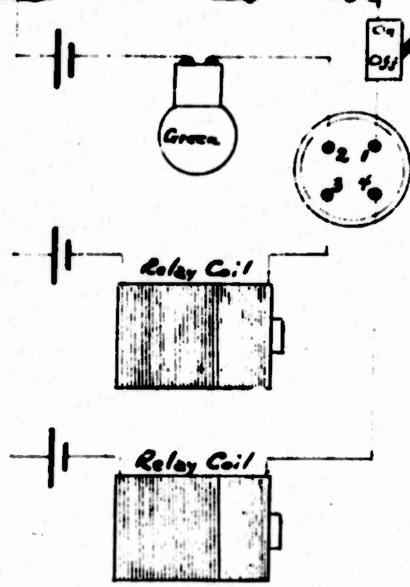

FIGURE 5

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ABSTRACT:

A description is given of an apparatus developed for the determination of carbon monoxide and air mixtures ranging in concentration from 0.01% to 0.1% and higher, if necessary. The principle of the apparatus is dependent upon the heat developed when carbon monoxide reacts with oxygen on a hopcalite surface. The apparatus is simple in construction, unusually easy to operate, entirely automatic in operation, and requires little servicing. Although it is limited in its sensitivity, the apparatus might well be used in a number of places where appreciable amounts of carbon monoxide might be found.

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